

STUDY OF THIN FILM LARGE AREA
PHOTOVOLTAIC SOLAR ENERGY CONVERTER

Second Quarterly Report
January 1, 1963 - March 31, 1963

Contract No. NAS7-203
National Aeronautics and Space Administration
Western Operations Office

CLEVITE
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ABSTRACT

This Second Quarterly Report discusses the work performed during the period January 1, 1963 through March 31, 1963.

A total of twenty-two evaporations have been performed under this contract, twelve being completed in the second quarter and yielding a total of 146 film samples ranging in size from 4 x 4 inches to 1 x 1 inch.

Improvements in processing of samples are described and data are tabulated to show how the average conversion efficiency has been raised from one-half percent to two percent as more parameters are identified and controlled. The principal cause of this increase is believed to be the cuprous oxide slurry technique developed in this laboratory. Single crystal cells processed in this manner have exhibited nominal efficiencies as high as nine percent - nearly twice that of crystal cells prepared by the prior electroplating process.

Spectral transmission curves are given for evaporated CdS films showing the effect on optical transmission of the barrier layer formed by the cuprous oxide slurry. Other optical measurements are discussed including the transmission and UV behavior of the plastic substrate material, the spectral energy distribution of our solar simulator, and some of the details of determining the conversion efficiency of solar cells.

Electrical measurements are mentioned briefly and it is pointed out that Hall effect and conductivity measurements will be added to the usual determinations of efficiency and rectifying characteristics. An experiment is described which shows that the barrier layer accounts for nearly all the electrical resistance in a CdS cell.

Progress in "wet chemical" methods of depositing CdS films is described as are preliminary film structure studies.

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1. INTRODUCTION

Present day photovoltaic solar energy converters are made of many small silicon cells each of which must be soldered into a series-parallel array to provide the required electrical power for a given satellite system. A typical silicon cell is approximately $1 \times 2 \times 0.05 \text{ cm}^3$ in size and has an efficiency of ten or fifteen percent; therefore, each cell delivers twenty or thirty milliwatts of power and many cells are required to power a satellite. Furthermore, each cell is very much thicker than its p-n junction; consequently, unnecessary weight is involved in a silicon solar cell array.

It is the purpose of this contract to develop a large area thin film photovoltaic solar energy converter. It is hoped eventually that cadmium sulfide cells one foot square and one or two mils thick will be produced, although for the present, smaller areas will be studied. The highest efficiency of presently available thin film cadmium sulfide cells is around three percent over relatively small areas, and although the density of cadmium sulfide is twice that of silicon, the thickness of a cadmium sulfide cell is only about one-tenth that of a silicon cell. Thus, large area cadmium sulfide cells would compare favorably on a weight-per-watt and cost-per-watt basis with silicon cells. Furthermore, cadmium sulfide film cells have been produced on flexible metal or high-temperature organic plastic substrates which represents a great potential improvement over the rigid backing required by single crystal silicon cells.

This report covers work done during the second quarter of this contract.

2. PRODUCTION OF VACUUM EVAPORATED FILMS

Twenty-two evaporations have been performed through March 31, 1963, yielding a total of 180 film samples ranging in size from 4 x 4 inches to 1 x 1

inches. Most of the samples have been 1 x 2 inches or 1 x 4 inches. Of these twenty-two evaporations, twelve have been completed in the present reporting period: two evaporations in January yielded eleven film samples, two evaporations in February yielded twenty film samples and eight evaporations in March yielded 146 samples.

2.1 Evaporant

It is known that the single crystal boules from which these films are evaporated are not uniformly doped: that the last grown end is richer in indium. Various experiments have been set up to determine whether it is best to use a particular portion of a boule, or whether the boule should be broken up into small pieces, the pieces mixed together, and distributed uniformly among the crucibles. Results so far are only tentative; it appears that the latter procedure is satisfactory, but other parameters have as much or greater influence on the quality of a finished cell.

Films described in this and earlier reports were made from boules A-27 through A-30 and boules T-1, TS-2, TS-3, T-4 and T-5. Boules A-27 through A-30 were grown from a $\text{CdS-In}_2\text{S}_3$ powder mix sintered in vacuo for one hour at 770°C and then in argon for approximately 20 hours at 985°C . Boule T-1 was grown from a similarly treated sintered mass, but boule T-4 was grown from a mix sintered in vacuo for 1.5 hours at 770°C and then in argon for 1.5 hours at 1225°C . Boule TS-2 was a sintered mass, similar to T-1 but not given the long heat treatment which promotes crystal growth. Boule TS-3 was a loss when the sintering furnace failed. Boule T-5 was similar to T-1.

Boules A-27 through A-30 were made prior to the start of this contract and pieces were used in many experiments performed in the preceding months. No record was kept to tell from which part of a boule a given chip was taken, so no comparison can be made with boule T-1. Accounting procedures were instituted at the start of this contract to provide such records and it is expected that as more films are produced significant correlation will be found between photovoltaic film quality and the boules, or parts of boules, from which the films are evaporated.

Films obtained from boule T-1 were generally poor rectifiers and low efficiency photovoltaic cells when processed. In fact, those processed by electroplating with Cu_2O were usually destroyed in the plating bath while those treated with the Cu_2O slurry had at best an efficiency of only 0.3 percent.

Sintered mass T-2 yielded badly spattered films which were not processed.

Films obtained from the first grown end of boule T-4 were very high resistance (about 1000 ohms per square) films and were not processed. Films obtained from the remainder of boule T-4 resulted in very poor photovoltaic cells. This is believed to be the result of the different method of growing the boule.

Boule T-5 yielded good films with efficiencies as high as 4.4% over areas as large as 4 cm^2 . Several evaporations were made from this boule and the quality of the resulting photovoltaic cells was found to depend strongly on the distance between the substrate and the evaporator. The best films were obtained when this distance was small, i. e., 5 inches.

2.2 Evaporator

A few experiments served to establish the superiority of the four-crucible evaporator described in an earlier report.⁽¹⁾ This evaporator has been considerably improved by the addition of fused quartz crucibles which contain the evaporant and are located within the heater coils. This prevents contamination of the charge by contact with the hot tantalum filament. A further improvement is a double walled quartz crucible with the tantalum heater contained in the annular space between the walls. The walls are sealed together at the upper end of the crucible. This completely encloses the hot tantalum in quartz. A tantalum foil radiation shield is placed around the crucible. A single crucible of this type is undergoing tests in the small vacuum system. If this crucible operates as expected, four of them will be employed in the large vacuum system.

⁽¹⁾ W. J. Deshotels and F. Augustine, "Study of Thin Film Large Area Photovoltaic Solar Energy Converter," First Quarterly Report, January 11, 1963, Contract No. NAS7-203.

2.3 Substrate

The substrates employed in the vacuum depositions are either pyrex glass or duPont H film. The pyrex glass is available in two thicknesses, 1/8 and 1/16 inch, and in area 4 x 4, 4 x 1 and 2 x 1 inch.⁽²⁾

An additional datum recently obtained for H film is its coefficient of thermal expansion. DuPont reports this to be $2.04 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$ between -14°C and $+38^{\circ}\text{C}$. This is an order of magnitude larger than the thermal expansion coefficient of CdS which is reported^(2, 3) as ranging from $2.4 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ at 0°C to $3.3 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ at 300°C when measured parallel to the C-axis and ranging from $4.0 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ at 0°C to $6.1 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ at 300°C when measured perpendicular to the c-axis.

2.4 Processing of Films

All films and crystal photovoltaic cells are now processed with the Cu_2O slurry technique described in the First Quarterly Report.⁽¹⁾ The process is being continually improved and consists now of painting the slurry onto the area to be processed, drying at a low temperature and washing off the excess with distilled water. The cell is then heated in air on a hotplate at 300°C for a short time: 5 seconds for crystal cells and up to 30 seconds for film cells.

A further improvement in film cell quality has been achieved by etching with HCl just before painting with the slurry. However, it appears to be necessary to heat the film to 300°C for 30 or 40 seconds before etching. It is not yet clear whether this strain relieves the film or simply degasses the film, but if the etch is done without heating, the film is likely to separate from the substrate.

One advantage of the slurry technique is that films which could not be electroplated with Cu_2O because of high film resistance can now be

(2) L. R. Shiozawa, et. al., "Research on II-VI Compound Semiconductors" Second Quarterly Report, August 1, 1962, Contract No. AF 33(657)-7399, Air Force Research Division, Air Research and Development Command, United States Air Force.

(3) Ibid., Fourth Quarterly Report, February 1, 1963.

processed successfully. Figure 1 shows the current-voltage characteristic of one of the first films treated with the Cu_2O slurry. This film has an efficiency of only 0.086 percent, but could not have been processed at all by electroplating because of its high resistance of 25 ohms per square. This was also the first relatively large area film (41 cm^2) produced under this contract. The high resistance accounts for the low efficiency.

2.5 Quality of Film Cells

There has been a steady improvement in the average quality of the evaporated film CdS photovoltaic cells. The large evaporator introduced new values for all of the film parameters and some time was required to learn to cope with the changes. Early film cells exhibited efficiencies ranging from one-half to one percent over areas of the order of 5 cm^2 and peak efficiencies greater than three percent over areas considerably less than 1 cm^2 . Present cells exhibit efficiencies of about two percent over areas of the order of 5 cm^2 with peak values of 4 percent over the same areas. It is tentatively concluded that this improvement is due primarily to the Cu_2O slurry process; to decreasing the distance between the substrate and evaporator crucible; to using evaporated metal (silver or gold) electrodes on the barrier layer instead of conducting silver paint; and to elimination of contamination of the CdS vapor by using the quartz crucibles described in Section 2.2. This does not, of course, imply that these are the only important parameters. Such quantities as composition of the charge, evaporating temperature, substrate temperature, treatment of substrate surface, etc. are important and have been proven so through experiment and experience. In recent evaporations, these latter quantities have been maintained reasonably constant while the former have been varied.

Table 1 lists some of the cells and their parameters which have led to these conclusions. It must be emphasized, however, that these are not final conclusions and experimentation in all parameters will be continued.

The current-voltage characteristics for a few of these film cells are shown in Figs. 2, 3, 4 and 5. Figure 2 is the curve for film cell 15-C and represents the poorest type of cell for which an efficiency can be obtained. Figure 3 shows the curve for cell 20-2 and is representative of early cells with

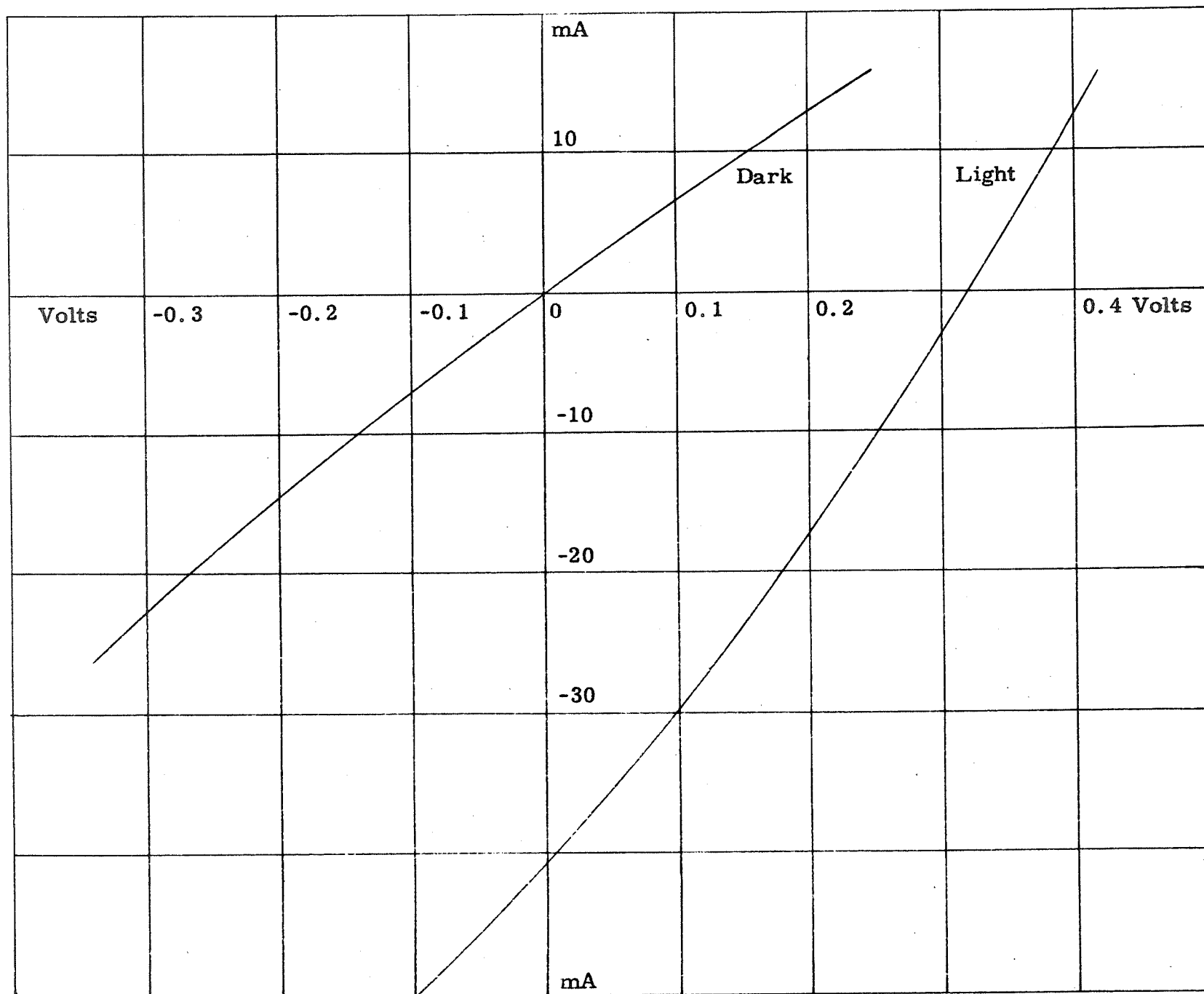


Figure 1. Current-Voltage Characteristic of Evaporated CdS Film Cell 3 CdS (A-27)G. Active Area: 41 cm^2 . Efficiency: 0.09%

Table 1. Typical Evaporated Film Cell Properties

Cell Designation	Active Area (cm ²)	Open Circuit Voltage (volts)	Short Circuit Current (amperes)	Substrate to Charge Distance (inches)	Collector Electrode	Boule From Which Charge Was Taken	Efficiency at Maximum Power Point	Comment
15-B-3	11.75	0.31	0.022	12	Ag paint	T-1	0.32	18-inch evaporator
15-C	10.5	0.18	0.006	12	Ag paint	T-1	0.1	18-inch evaporator
16-3-g	6.7	0.38	0.035	9	Ag paint	T-4	0.6	18-inch evaporator Boule:See Sec.2.1
16-3-e	11	0.36	0.052	9	Ag paint	T-4	0.6	18-inch evaporator Boule:See Sec.2.1
17-a	11	0.35	0.027	5	Ag paint	T-5	0.3	12-inch evaporator
18-3-F	9.7	0.31	0.018	6	Ag paint	T-5	0.1	18-inch evaporator
18-3-E	11	0.33	0.030	6	Ag paint	T-5	0.3	18-inch evaporator
20-3	5.25	0.45	0.032	5	Ag paint	T-5	0.7	12-inch evaporator
20-2	7	0.42	0.026	5	evaporated gold	T-5	0.5	12-inch evaporator
21-4-E	6.6	0.45	0.056	6.5	Ag paint	T-5	2.1	18-inch evaporator
21-4-C	7	0.42	0.072	6.5	evaporated gold	T-5	2.1	18-inch evaporator
21-4-H	7.4	0.43	0.068	6.5	evaporated gold	T-5	1.9	18-inch evaporator
21-4-B	3.75	0.45	0.068	6.5	evaporated gold	T-5	4.4	18-inch evaporator
21-4	3 mm dia.	0.45	0.0013	6.5	Ag paint	T-5	3.9	18-inch evaporator
21-4-G	6.5	0.29	0.084	6.5	evaporated silver	T-5	2.1	18-inch evaporator

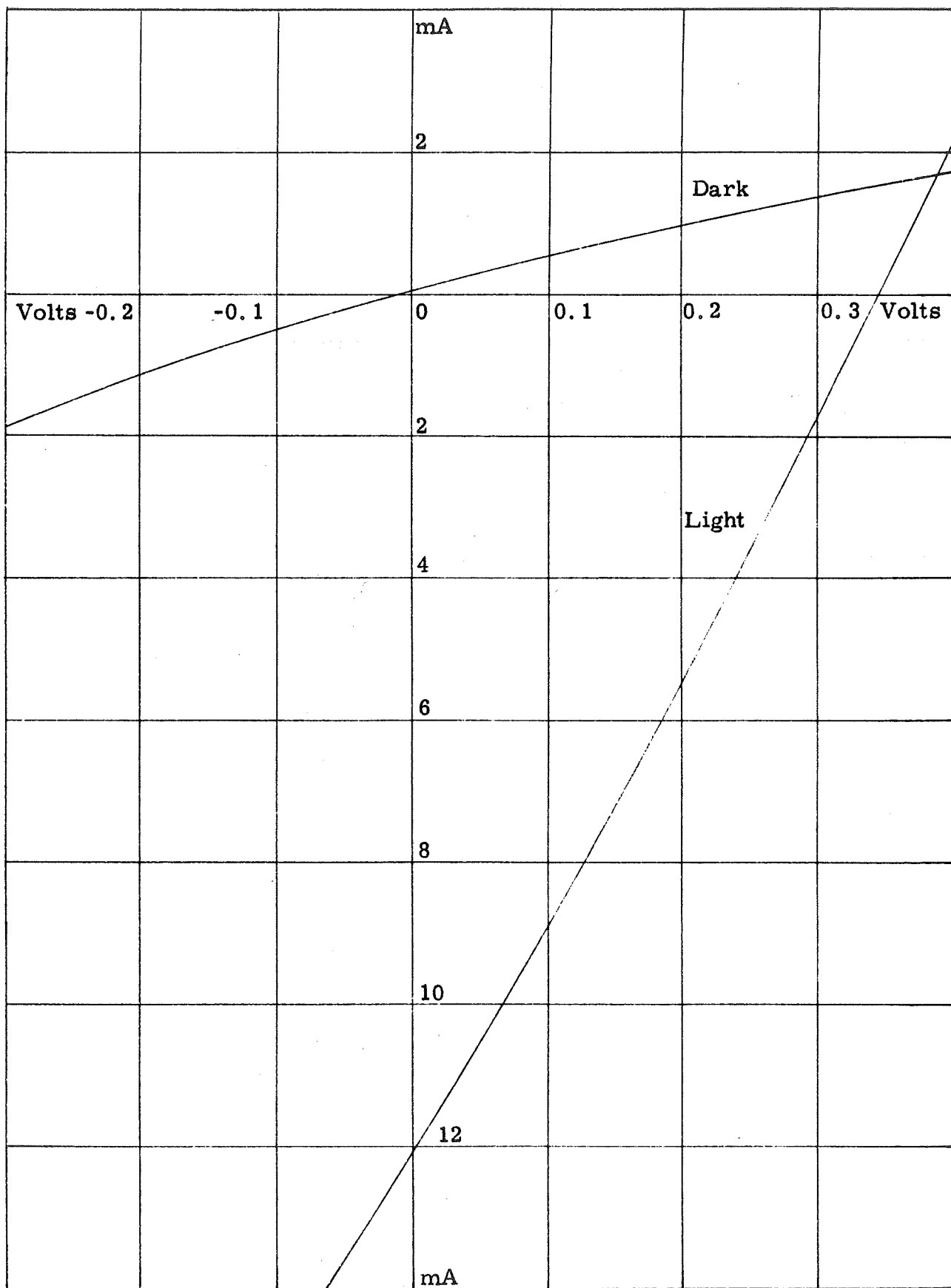


Figure 2. Current-Voltage Characteristic of Evaporated CdS Film
Cell 15-C. Active Area: 10.5 cm^2 . Efficiency: 0.1%

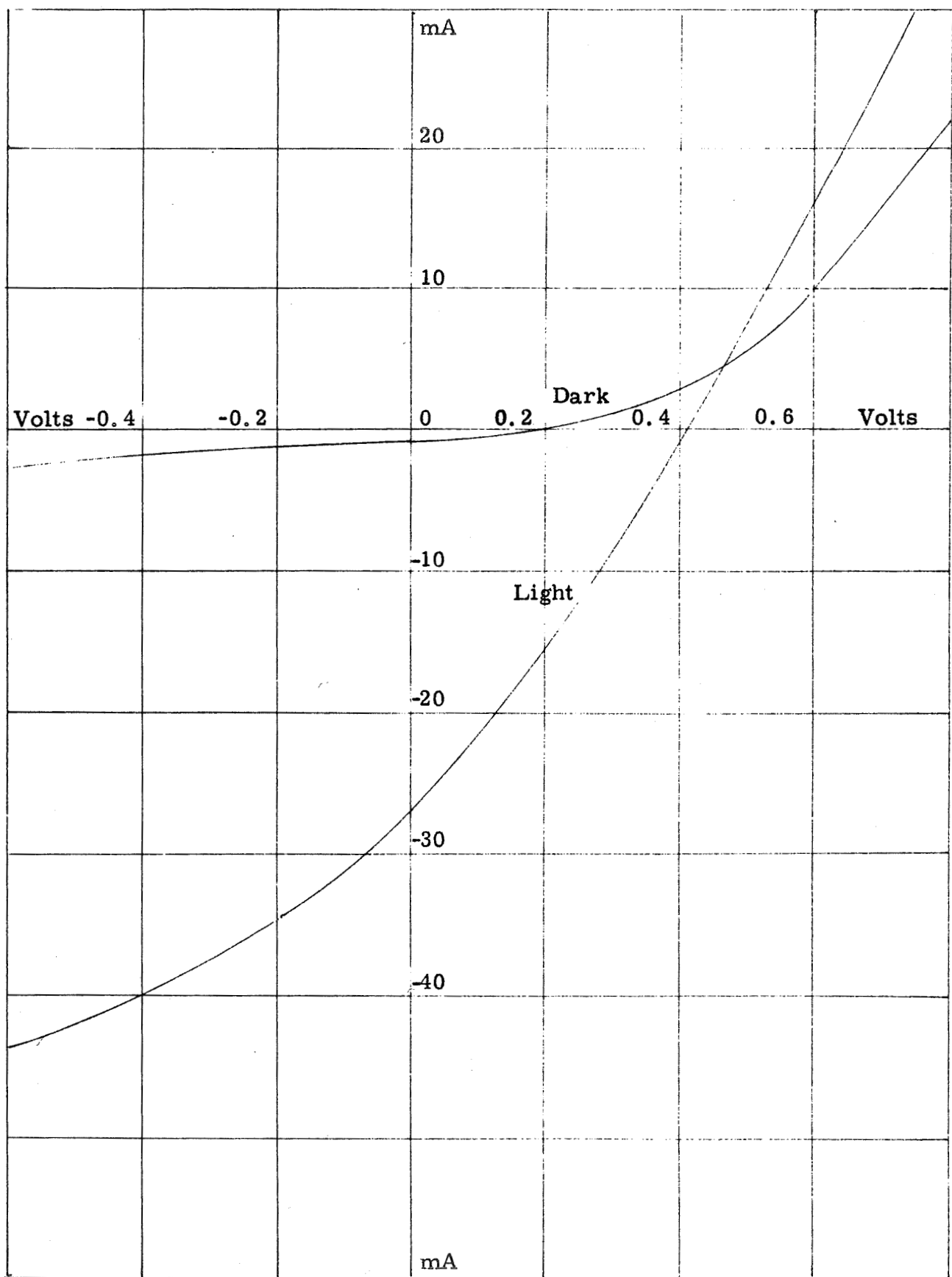


Figure 3. Current-Voltage Characteristic of Evaporated CdS Film Cell 20-2.
Active Area: 7 cm². Efficiency: 0.5%

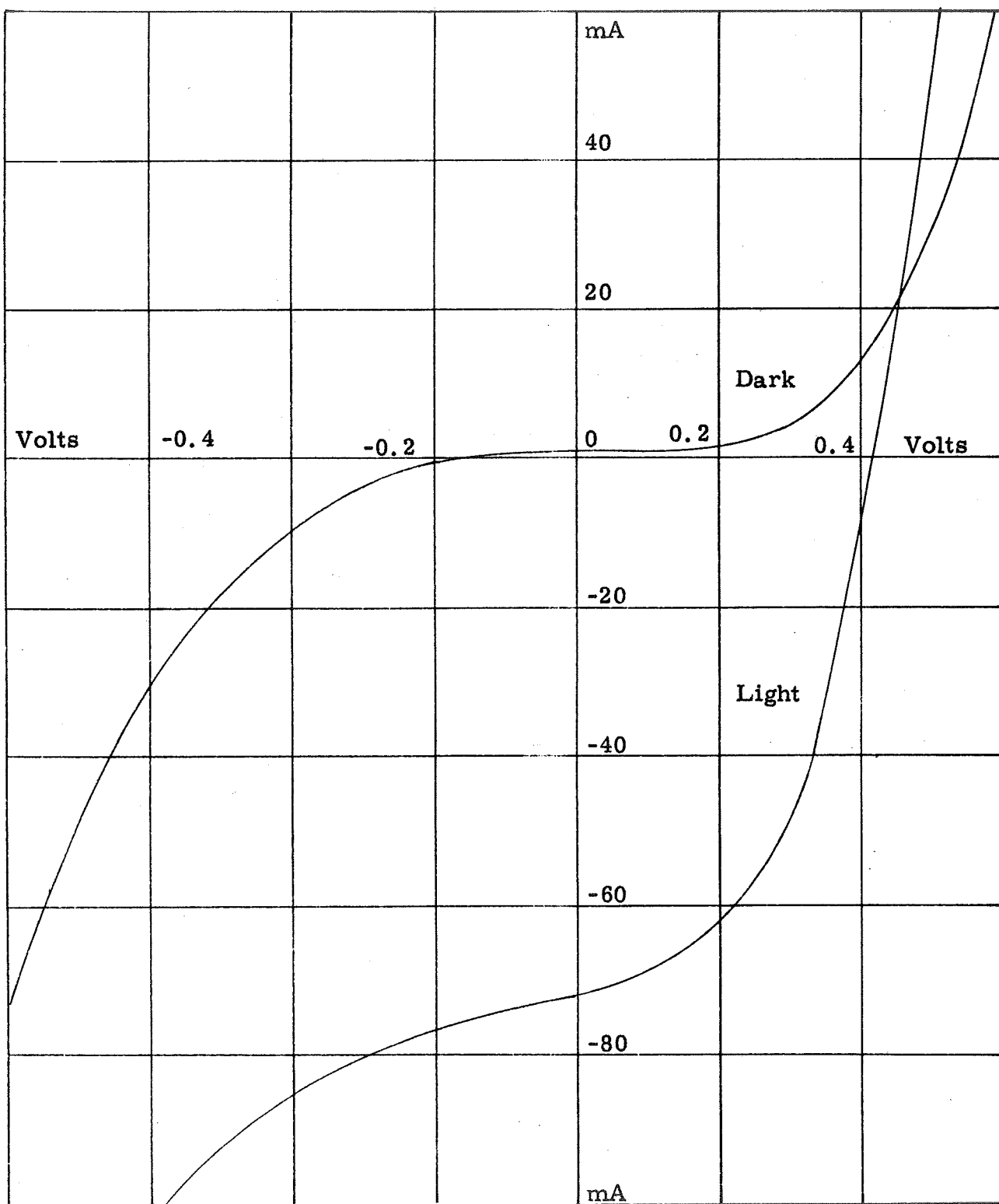


Figure 4. Current-Voltage Characteristic of Evaporated CdS Film Cell
21-4-C. Active Area: 7 cm². Efficiency: 2.1%

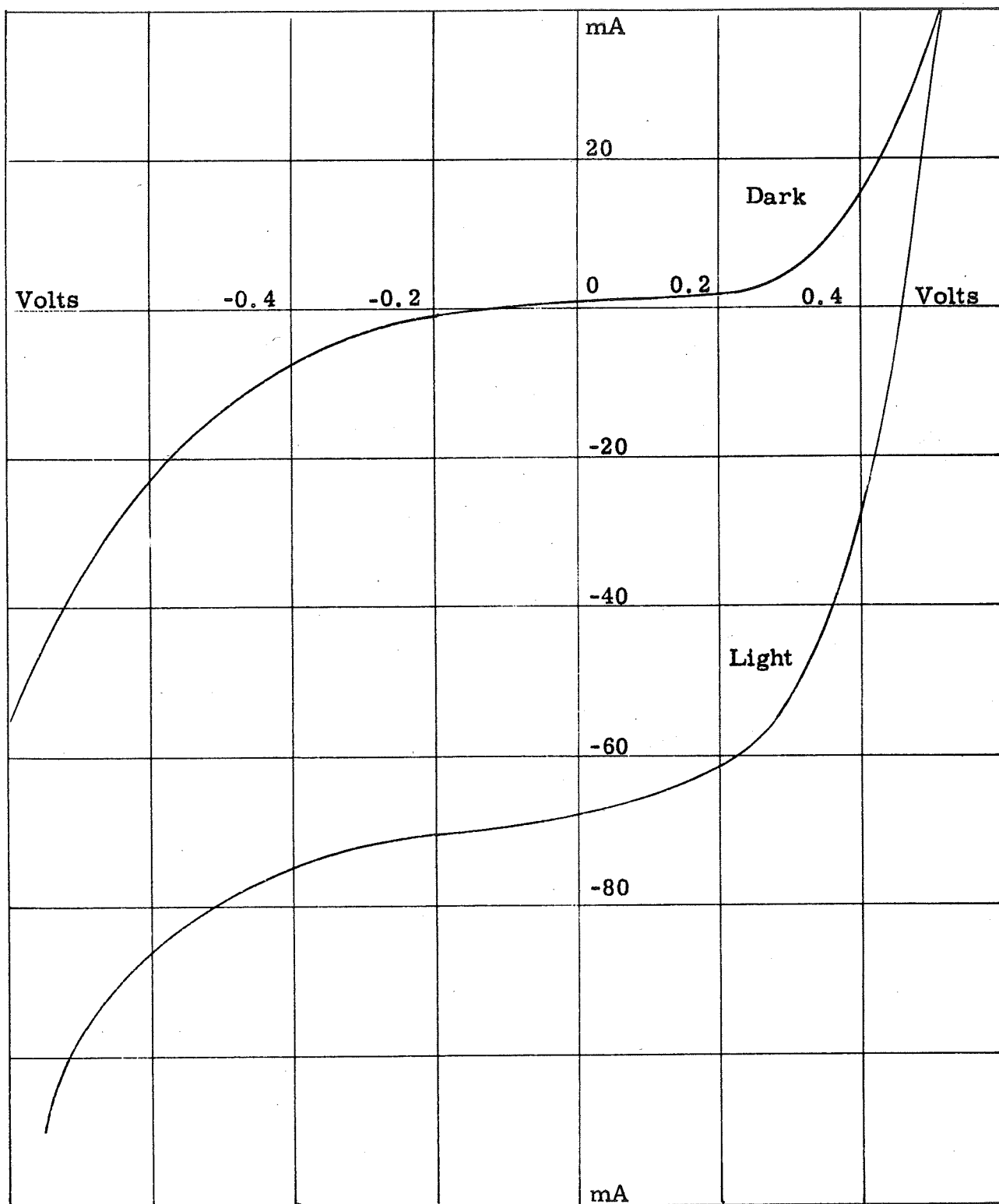


Figure 5. Current-Voltage Characteristic of Evaporated CdS Film Cell 21-4-B. Active Area: 3.75 cm². Efficiency: 4.4%

average efficiencies of about one half percent. Figure 4 is the curve for cell 21-4-C and is typical of the presently available two percent cells while Fig. 5 shows the curve for cell 21-4-B which represents the highest film cell efficiency obtained so far.

2.6 Single Crystal Photovoltaic Cells

A number of single crystal CdS photovoltaic cells were prepared to study the effectiveness of the cuprous oxide slurry process. Table 2 lists a few of these along with their open circuit voltages, short circuit currents, active areas and efficiencies. The current-voltage curve for cell 12 CdS (A-27) is shown in Fig. 6.

Table 2. Single Crystal CdS Photovoltaic Cells
Processed with Cuprous Oxide Slurry

Cell Designation	Active Area (cm ²)	Open Circuit Voltage (volts)	Short Circuit Current (amperes)	Efficiency at Maximum Power Point
3CdS(A-27)	1.7	0.55	0.044	7.0%
12CdS(A-27)	.32	0.52	0.0168	9.4%
13CdS(A-27)	.32	0.54	0.013	8.3%
14CdS(A-27)	.75	0.52	0.012	5.8%
15CdS(A-27)	.4	0.52	0.0096	5.5%

These efficiencies are significantly higher than previously reported and indicate the success of the cuprous oxide slurry process for obtaining CdS photovoltaic cells.

3. MEASUREMENTS

3.1 Spectral Transmission of CdS and DuPont H Film

Spectral transmission measurements are obtained by the sample-in-sample-out technique using a Bausch & Lomb grating monochromator having a 500 mm focal length and a 10 x 10 cm², 600 groove/mm grating blazed at

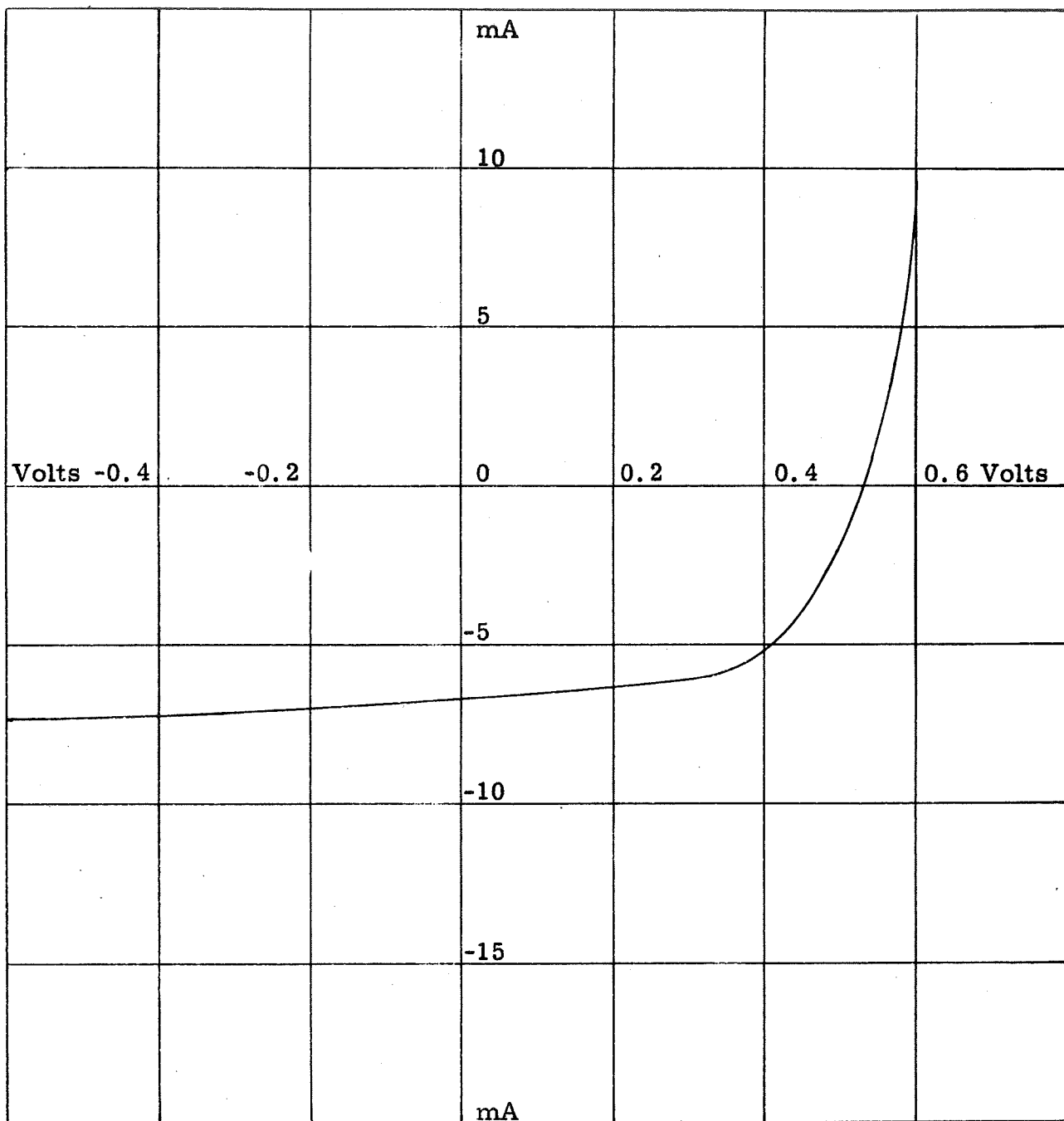
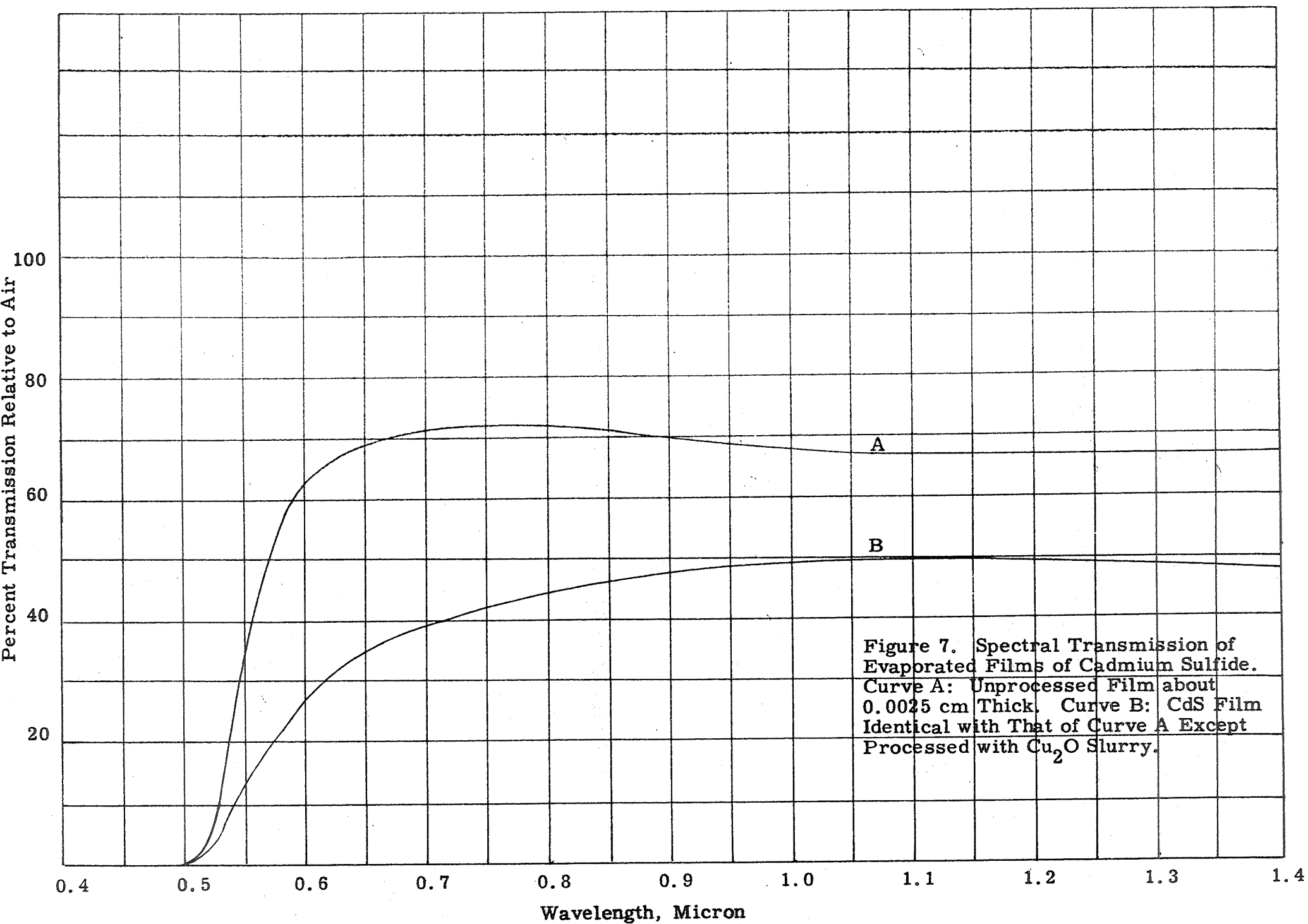


Figure 6. Current-Voltage Characteristic of Single Crystal CdS Cell 12 CdS (A-27). Active Area: 0.32 cm^2 . Efficiency: 9.4%

5000 Å in the first order. Dispersion of the instrument is 33 Å per mm in the first order. The range of the instrument is 0.2 to 1.4 microns. Input light is chopped at 13 cps. The chopper shaft carries a cam which operates a SPDT micro-switch at the chopper frequency. This permits the employment of either of two detectors: a lead sulfide detector (Eastman Kodak Co. Type N-1 Ektron Detector, sensitive area, 2 x 2 mm), or a Perkin-Elmer thermocouple, feeding into the amplifier and recorder borrowed from a Perkin-Elmer infrared monochromator. This arrangement also provides for continuously recording a spectrum by driving the wavelength drum of the B & L Monochromator with a clock motor geared so that 2.5 inches of recorder chart travel correspond to a 0.1 micron interval. Normally the spectrum is run from 1.4 to 0.3 micron, the longer wavelengths being recorded first. The bandwidth is determined by the slit width. The recorded trace represents detector output signal vs wavelength. A Corning glass filter No. 2-64 is placed in front of the entrance slit when operating in the first order between 1.4 and 0.7 micron. This clears the first order spectrum of second order 0.7 to 0.35 micron radiation. The filter is removed when operating between 0.7 and 0.35 micron. The glass water filter and glass lamp bulb effectively eliminate ultraviolet radiation below 0.35 micron. The sample-in-sample-out method gives highly repeatable results. The continuous recording gives a spread of about 5 percent in successive recordings.

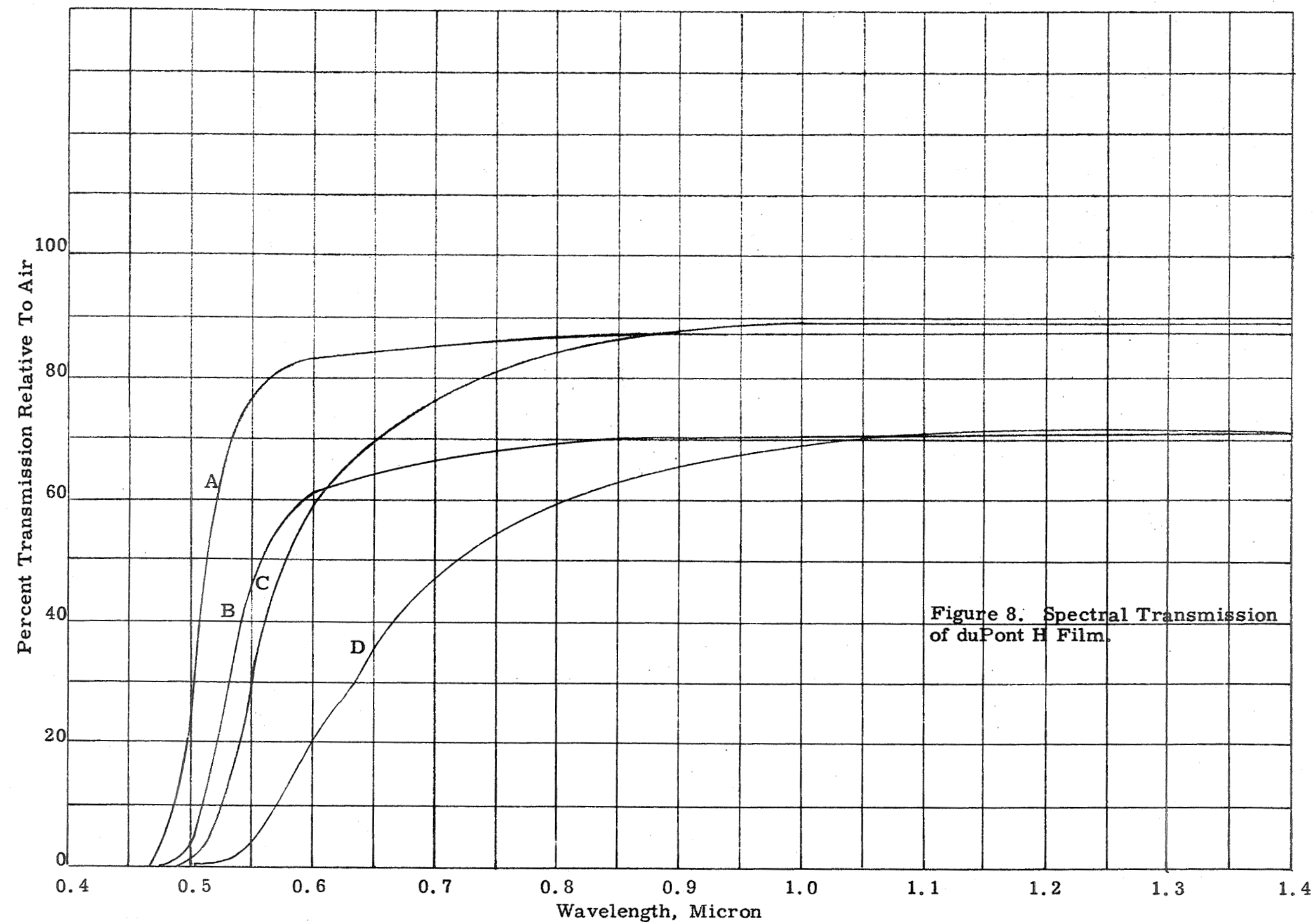
The curves shown in Figure 7 are the spectral transmission, relative to air, of two evaporated films of indium doped cadmium sulfide on glass substrates. Curve A is for an unprocessed film about 0.0025 cm thick. The absorption edge is not nearly so well defined as in single crystal samples. Curve B is the transmission of a film identical to that of Curve A (the films were evaporated simultaneously and are adjacent parts of the same substrate) except that it was processed by painting with precipitated cuprous oxide, heated in air at 300°C for a few seconds after which the excess oxide was brushed off. It will be interesting to compare the curves of Figure 7 with those of conventionally processed films and crystals, as well as unprocessed crystals. These measurements will be performed in the next reporting period.



The curves in Figure 8 are the spectral transmission, relative to air, of four samples of duPont H film. Curve A was obtained from a single thickness of H film, 0.0062 cm thick. This film has a yellow color similar to that of CdS. Curve B was obtained from a triple thickness of the same H film. Curve C is the transmission of a single thickness of H film, 0.0118 cm thick. This film has a red-orange color, much darker than the thinner H film. Curve D is a triple thickness of the latter film. It is interesting to note the somewhat greater transparency of the darker film in the near infrared region of the spectrum. Comparing Figs. 7 and 8, one concludes that in single thicknesses, the light, yellow, H film must be employed as a substrate for backwall CdS photovoltaic films.

3.2 Solar Simulator

Extensive measurements have been made of the spectral distribution of radiant energy from the lamps used in the solar simulator. Before describing the experiment or discussing its results, it would be well to mention some of the ideas underlying the measurement of cell efficiency. The efficiency is defined straightforwardly as the ratio of the electrical output power of the cell at its maximum power point to the total radiant input power. The input power, for the present application, is sunlight. The output power is simply measured. The input power is decidedly difficult to measure - or even define. For one thing, it is not convenient to use sunlight as a power source, for, when there is any sunlight at all, it is always in a state of modulation: by clouds, smoke, haze, and the angle of elevation, to say nothing of the fact that sunlight must penetrate the earth's inconstant atmosphere before it is generally available. Most experimenters find it convenient to use a sun simulator, usually a tungsten lamp, which, of course, must eventually be compared to sunlight. For surface applications one may fall back on the monumental work of the Smithsonian Institution which has measured the intensity of sunlight at the earth's surface for a period of more than 50 years and determined that the solar constant, i. e. the integrated intensity of solar radiation, varies periodically with an amplitude of approximately ± 3.5 percent.



Until recently, the value of the solar constant outside the earth's atmosphere was very doubtful. Until 1954, the Smithsonian Institution⁽⁴⁾ relied principally on the value deduced by Moon⁽⁵⁾ in 1940. This was 1.896 pyron (1 pyron = 1 cal cm⁻²-min⁻¹). The advent of high altitude rockets in scientific work permitted Johnson⁽⁶⁾ in 1954 to assimilate data from a number of sources,⁽⁷⁾ including those mentioned above, and to conclude the value of the solar constant outside the earth's atmosphere is 2.00 pyrons. The spectral distribution of solar radiation outside the atmosphere is shown in Fig. 9. These curves compare Johnson's with the Smithsonian-Moon (1954) curve. The ultraviolet portion of the radiation accounts for most of the difference between the 1940 and 1954 values of the solar constant. The curves shown here differ from Moon's 1940 curve in that Moon brought his curve to zero at $\lambda = 0.29$ micron. The portion of the curve for wavelengths longer than about 0.60 micron follow very closely the 6000°K blackbody curve. According to Johnson (also Moon, generally), about 9 percent of the sun's total radiated energy falls in the region lying between 0.22 and 0.40 microns, and about 15 percent of the energy is found at wavelengths greater than 1.4 micron. (Johnson's data extend to 7.0 micron; Moon's and the Smithsonian Institute's data extend only to 5.0 micron.)

Returning now to the measurement of solar cell efficiency, one may well ask which value of the solar constant should be employed in the calculation? There seems little doubt that for terrestrial operation, the averaged value determined by the Smithsonian Institution is as good as any available; or one may simply wait for a clear sunny day and measure the cell's efficiency at some convenient time, say high noon on a building roof or convenient hill. This could set a sort of interim standard involving a particular cell, which if its

(4) W. E. Forsythe, "Smithsonian Physical Tables," (Smithsonian Institute, Washington, D. C., 1954), 9th Ed., Tables 808, 810, 813, pp. 719-22.

(5) P. Moon, "Proposed Standard Solar Radiation Curves for Engineering Use," J. Franklin Institute, 230, 583-618 (1940).

(6) Francis S. Johnson, "The Solar Constant," J. Meteorology, 11, 431-39, (December, 1954).

(7) L. D. Dunkelman & R. Scolnik, "Solar Spectral Irradiance and Vertical Atmospheric Attenuation in the Visible and Ultraviolet," J. Opt. Soc. Am. 49, 356-67 (April, 1959).

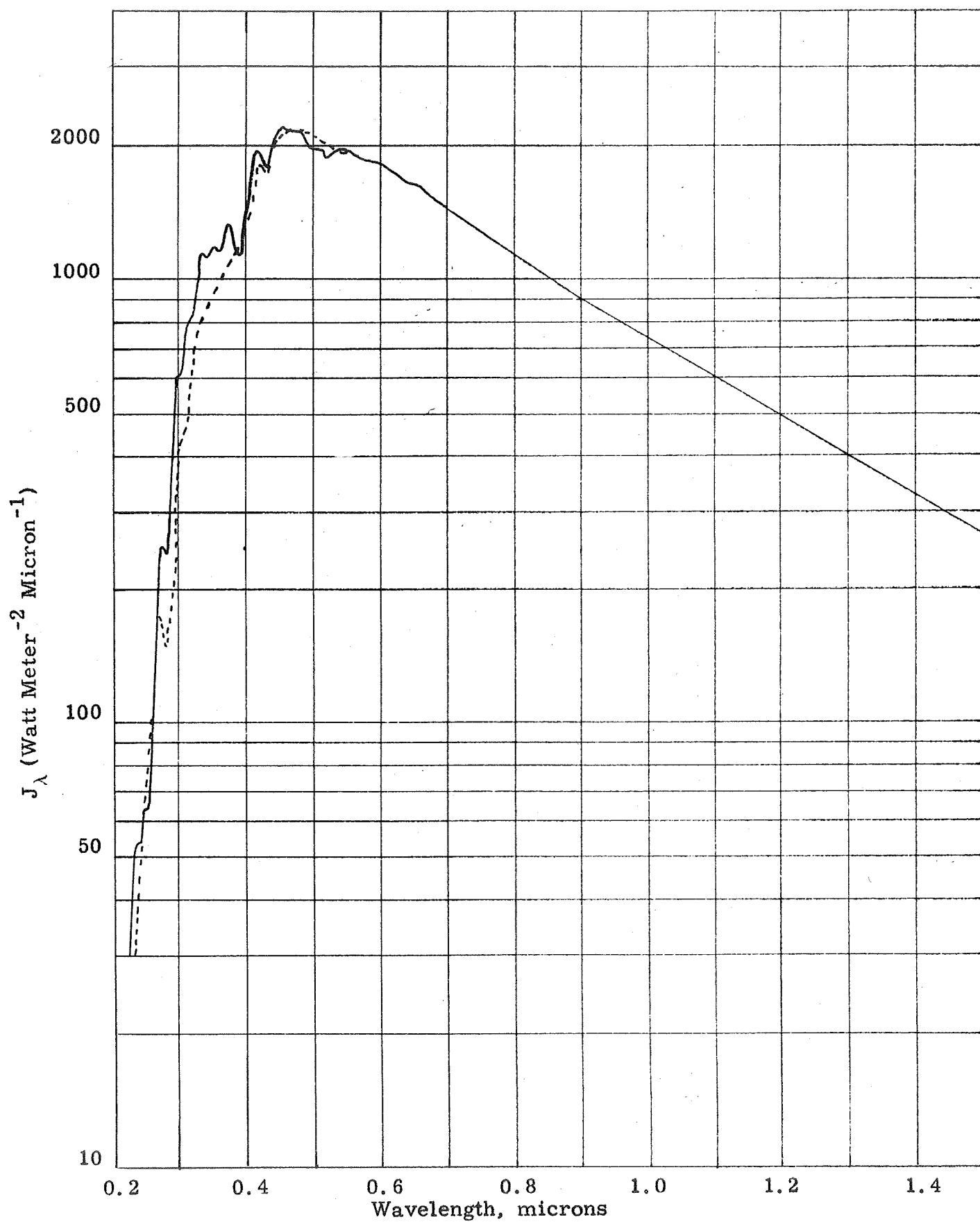


Figure 9. Spectral Distribution of Solar Energy Outside Earth's Atmosphere. Solid Curve According to F. S. Johnson (1954). Dotted Curve According to Moon-Smithsonian Institution (1940-1954).

properties remain unchanged, can be used as a criterion for all other cells under investigation. For extra-terrestrial operation, the problem is not so simply resolved. For one thing, the question arises: "Does one use the total incident solar radiation, i. e. 2.00 pyrons or does one use only that portion of the sun's radiation which is active in producing the photovoltaic effect in a particular solar cell?" The latter procedure is enticing as it permits one to claim a higher cell efficiency than would be possible if the total incident energy (2.00 pyrons) were used in the calculation of efficiency. In this regard, it is interesting to note that some silicon solar cell manufacturers use a tungsten lamp with an intensity of 100 mw-cm^{-2} (about 1.43 pyrons) to calibrate Si solar standards. Undoubtedly, this is based in turn on actual sunlight measurements. Probably the least equivocal solution is to assume Johnson's value for the solar constant and base all efficiency measurements on it. This could be confirmed, in time, by actually measuring the efficiency of a cell in an orbiting laboratory.

In the meantime, lacking an agreed-upon standard (and until summer, lacking natural sunlight) this laboratory will continue to use a 3400°K tungsten lamp and 0.25-inch water filter. The spectral distribution of this arrangement was measured in a manner similar to the spectral transmission measurements described in Section 3.1.

A General Electric Company PH/RFL2 Photoflood Lamp nominally rated at 120 V and 500 w with a filament color temperature of 3400°K is placed a few inches behind a fan cooled water filter 0.25 inch thick. The light is chopped at 13 cps by a rotating sector disc, passes through a Bausch & Lomb grating monochromator, and is detected by a Perkin Elmer thermocouple. The signal from the thermocouple is amplified, rectified and recorded on a strip chart recorder. The slits were normally opened to 1.0 mm.

To compare a trace of the spectral distribution of the photoflood lamp with that of sunlight, several preliminary steps are necessary. First, the experimental trace has an abrupt discontinuity at $\lambda = 0.7$ micron due to the removal of the Corning filter. Therefore, the two halves of the curve must be joined by moving the portion of the curve contained between 0.7 and 0.35 micron parallel to itself until the 0.7 micron ends match. This is most easily

accomplished by copying the two sections on a single strip of chart paper. Next, a planimeter is used to determine the area under the experimental curve. This area is

$$A = \int_{\lambda_1}^{\lambda_2} S_{\lambda} d\lambda, \quad (1)$$

where S_{λ} is the ordinate of the trace at wavelength λ and is proportional to the energy detected by the thermocouple in the wavelength interval $d\lambda$. The area A is proportional to the total power density E (watt meter⁻²) radiated by the lamp, i. e.

$$E = kA. \quad (2)$$

This determines k which is simply the power density per unit area under the experimental curve with dimension watt meter⁻² inch⁻². The inch⁻² comes from expressing the area under the curve A in square inches. The ordinate S_{λ} of the experimental curve, defined above, is measured in inches on the chart paper, and must be multiplied by the number of chart inches contained in a unit wavelength interval, the scale factor, to obtain a strip of area S_{λ} high and unit wavelength interval wide. This in turn must be multiplied by the constant k from Eq. (2) which relates the power density E to the area under the curve A . This product is

$$J_{\lambda} = S_{\lambda} \text{ (inches) } \times \text{scale factor (inch/micron) } \times k \text{ (watt m}^{-2}\text{)}, \quad (3)$$

giving J_{λ} the dimensions watt-meter⁻²-micron⁻¹.

Combining Eqs. (1), (2) and (3),

$$E = \int_{\lambda_1}^{\lambda_2} J_{\lambda} d\lambda. \quad (4)$$

For the chart and wavelength drive speeds available in the present set-up, the scale factor is 25 inch/micron. This leaves only the power density term E to be determined, and as it turns out, this is rather arbitrary. As long as the filament temperature, amplifier gain, thermocouple position and slit width remain constant, E simply determines the size of the ordinate scale for the spectral distribution. If the spectral distribution being measured were that of sunlight, E would be automatically determined and equal to the solar constant. In the present instance, however, E is completely arbitrary, for the spectral distribution of the photoflood lamp is determined only by its filament temperature and not by its absolute intensity. Therefore, in order to make a comparison of the lamp with sunlight, E is chosen to be that fraction of the solar constant corresponding to radiation covering the same wavelength range as the photoflood lamp. Since the lamp does not radiate significant energy below 0.3 micron and since the monochromator does not pass wavelengths longer than 1.4 micron, the value of the solar constant corresponding to this interval is chosen. This is 1153 watt m^{-2} (Moon's data) and all the spectral distribution curves are normalized to this value. (Johnson's data give 1176 watt m^{-2} for this interval.) Typical spectral distribution curves for the GE PH/RFL2 photoflood lamp are shown in Fig. 10 which compares curves for the lamp plus one-quarter and one-half inch thick water filters with Moon's proposed solar distribution curve. The area under the upper lamp curve is the same as that under Moon's curve. Other curves have been obtained with the lamp operated at 135 V instead of 120 V. No significant shift in the wavelength corresponding to the peak of the curve was observed. Lowering the intensity of the lamp from $1153 \text{ watt meter}^{-2}$ to $900 \text{ watt meter}^{-2}$ (increasing distance between lamp and monochromator) brings the portion of the curve between 0.65 and 1.1 micron into very close juxtaposition with the solar curve.

3.3 Uv Irradiation of H Film

A sample of duPont's H film has been exposed to a quartz mercury arc lamp for a total of 54 hours. The total energy incident upon the sample was $2 \times 10^4 \text{ joule cm}^{-2}$. There was no visible effect on the sample and no embrittlement. The spectral transmission of this sample was measured and compared with that of the sample before irradiation. No significant change was observed.

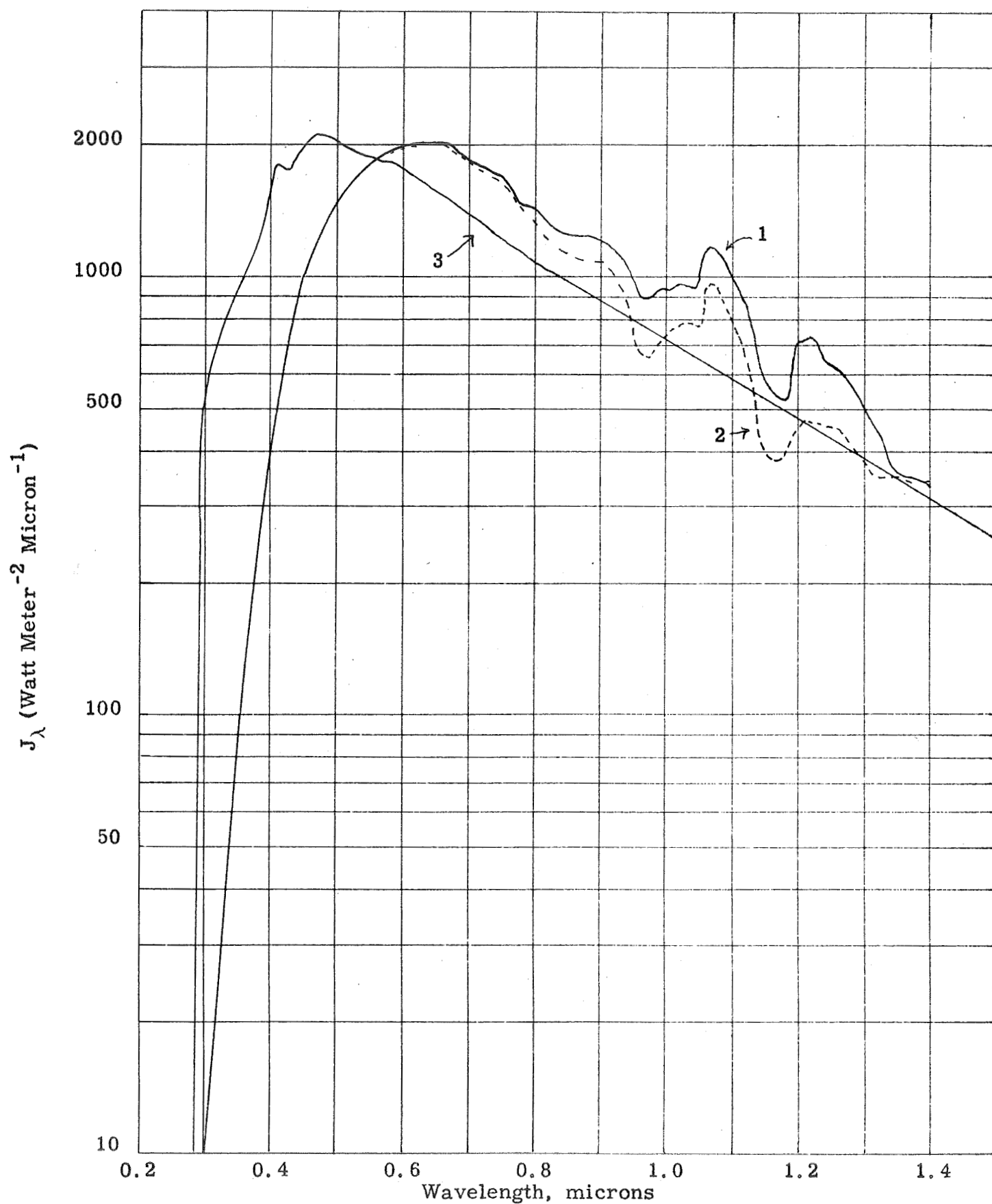


Figure 10. Radiant Energy Spectral Distribution of General Electric PH/RFL 2 Lamp Operated at 120 v. 1. Lamp plus 1/4" Thick Water Filter. 2. Lamp plus 1/2" Thick Water Filter. 3. Moon's Solar Energy Spectral Distribution Curve.

The following companies have been contacted regarding possible plastic film substrates for CdS solar cells: E. I. duPont de Nemours and Co., General Chemical Division of Allied Chemical Corporation, Pennsalt Chemicals Corporation, and Minnesota Mining and Manufacturing Company.

3.4 Electrical Measurements

The principal electrical measurements made on each cell are those which result in the dark and light current-voltage characteristics and cell efficiency. These measurements were described in some detail in the First Quarterly Report. In addition to these, other measurement procedures have been established which will provide much needed information concerning, for example, carrier type and concentration in bulk and film samples, conductivity of the various layers comprising a film cell, and diode characteristics of film and crystal cells.

Thus, Hall effect and conductivity measurements will become a regular routine. At present, preliminary measurements are made only at room temperature in order to establish suitable designs for sample holders, jigs, etc. Shortly, these measurements will be extended to other temperatures. The automatic recording apparatus for plotting I-V curves has been modified to provide independent current and voltage contacts so that true potentials may be measured at any point on a cell. These measurements will supply data on the conductivities of the CdS, Cu_2O and collector electrode layers of a cell. If temperature can be varied over a sufficient range, it should be possible to determine activation energies for the CdS and barrier layers in a photovoltaic cell.

Details of these measurements will be given in a later report after the permanent apparatus arrangements have been established.

It is possible to report, now, however, that the various layers in one completed cell appear to form equipotential planes or surfaces indicating that there are no large variations in conductivity of the layers. This has yet to be compared with the local response of the cell. This cell was prepared by coating a rectangular area of the CdS surface with the Cu_2O slurry and heating. A silver collector electrode was evaporated onto the Cu_2O surface without

removing the excess powder. Contact to the CdS was made by soldering two stripes of indium along the long edges of the CdS layer being careful to keep the indium away from the oxide layer. Indium tipped probes to one of these stripes and the silver electrode formed the current contacts. Another pair of indium tipped voltage probes was used to probe the various layers, measuring the potential at a given point relative to the indium stripe. The potential at various points on the silver layer was found to be essentially constant indicating an equipotential surface. The potentials measured at various points on the exposed border of Cu_2O were also constant as were the potentials measured at various points on the exposed CdS layer. Thus, the three layers, Ag, Cu_2O and CdS were all equipotential surfaces. From the values of potential obtained and the current (3 mA) flowing through the cell (the cell was weakly illuminated with room light) the resistances through the various layers in a direction perpendicular to the layer could be estimated. The greatest potential drop, about 100 mV, was measured between the CdS and Cu_2O layers indicating a surface resistivity of about 300 ohm cm^2 for the interface between the two. Similarly, the surface resistivity of the Ag- Cu_2O interface was about 30 ohm cm^2 and for the CdS-indium stripe the surface resistivity was negligible. Recalling that the excess Cu_2O layer was not removed from this cell after processing, it is clear that the 330 ohm cm^2 measured includes the resistivity of this excess material as well as that of the actual barrier layer.

The following experiment was performed to determine whether the major part of the resistance was due to the barrier layer or the excess material: a clean glass plate was painted with the Cu_2O slurry and processed in the usual fashion. The resulting layer was 4.5 cm long by about 1.1 cm wide and about 30 microns thick. As nearly as possible this layer was exactly like the layer on the CdS cell described above. Indium and silver paint were used to make contact to the ends of the strip. A voltage was applied to these ends and the current and potential measured. The resistivity of the strip was found to be about $9 \times 10^3 \text{ ohm-cm}$ giving a surface resistivity of about 28 ohm-cm^2 . This is less than one tenth the value obtained for the CdS cell and so one concludes that the greater part of the resistance lies in the barrier layer between the Cu_2O and CdS.

Another evaporated film, unprocessed, was used for Hall effect and conductivity measurements. Contacts to the CdS film were indium amalgam and some difficulty was encountered due to contact resistance to the amalgam. However, a crude measurement was obtained with the following results: resistivity, 0.012 ohm-cm; carrier concentration, n-type, $2.9 \times 10^{19} \text{ cm}^{-3}$; mobility, $18 \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}$. A more suitable sample holder is being made and will eliminate the difficulties experienced in making electrical contact to the film.

4. ALTERNATE METHODS OF PRODUCING FILMS

The "wet chemistry" approach to producing CdS films has been rather encouraging. A spray process was developed which deposits hard, adherent films of CdS on heated substrates. A single gun spray was used. Hydrogen sulfide gas was forced through the nozzle and entrained cadmium chloride (or nitrate) solution from a reservoir. It is assumed the reaction, precipitation of CdS, started at the instant of mixing and continued even after striking the heated substrate. Thus some CdS was formed in situ and it is believed that this formed the observed deposit. The substrate was in a muffle furnace with the temperature maintained at 400°C to 600°C. Dry nitrogen was passed through the muffle to exclude as much atmospheric oxygen as possible. In the early phases, no attempt was made to dope the films. The deposits were hard, yellow, had high resistance, and did not exhibit a photovoltaic effect.

Indium doping was attempted by adding indium chloride or nitrate to the cadmium solution. This produced films with resistances as low as 10 ohms (between probes 1 cm apart) but no photovoltaic effect was observed.

Gallium was tried next, resulting in relatively high resistance films, i. e. higher than the indium doped film but lower than the undoped films, and a photovoltaic effect was observed. Typically, the open circuit voltage was about 0.4 volt, but resistances of the order of one megohm were encountered.

It became apparent that the high substrate temperature was causing some sintering of the deposited film. This led to a review of S. M. Thomsen's patent⁽⁸⁾

⁽⁸⁾ S. M. Thomsen, "Sintered Photoconducting Layers," U.S. Patent No. 2,765,385, issued October 2, 1956.

for producing photoconducting CdS films by a sinter technique. His slurry recipe was followed with variations, i. e. Ga and In were substituted for Cu, and films produced in this manner always showed a photovoltaic effect with typical values of 0.3 volt and 10 microamp obtained for the open circuit voltage and short circuit current respectively on areas about 1/4 inch in diameter.

Many other variations have been explored, including the use of CdCl_2 as a flux to promote grain growth after deposition. This work will continue.

5. FILM STRUCTURE STUDIES

X-ray diffraction methods are being developed for basic study of polycrystalline thin films. Crystallite size and orientation in CdS films have apparently been subjected to little such previous investigation. These first experiments were therefore somewhat of a reconnaissance nature.

Both back and forward reflection Laue photographs were made; these were found to yield comparatively little information. The North American Philips diffractometer was therefore used most extensively. When used in the standard fashion, this camera "sees" only the Bragg-reflecting lattice planes that lie parallel to the plane of the film itself; diffraction intensities are measured with either a Geiger-Muller or a scintillation counter and recorded on a strip chart. If such a film is composed of crystallites oriented completely randomly, the resulting series of peaks on the chart recorder will have intensities and reflection angles identical (with certain corrections due to camera geometry) to those measured by other techniques. If, however, there is any degree of preferred orientation, the ratios of the diffraction peak intensities to each other will be altered.

When such examination was made of several CdS evaporated films, it was found in every case that strong orientation effects have taken place such that all the CdS crystallites have their C-axes not far from perpendicular to the plane of the film. Most of the subsequent work during the period was exerted toward means of quantitatively measuring and describing this orientation.

It was first to be noted that it was observed that of all the lattice planes detected as being parallel to the film plane, none allow the C-axis of the

corresponding crystallites to be more than 32° from the normal to the film plane. This extreme is observed only when the direction of evaporation is oblique (about 15° from the vertical) to the glass substrate surface; when the sublimed CdS atoms or molecules arrive perpendicularly, the C-axes virtually all lie within 15° from that direction. The diffractometer was then modified to scan through an angle of 13° on either side of the vertical while "seeing" only the (0002) basal reflection; the orientation of the C-axes (which are perpendicular to the (0002) planes) was found to be shifted toward the direction of sublimation. Within this 26° of viewing angle, it was also found that a sprayed film is strongly oriented with (0002) planes parallel to the glass substrate. At 10° on either side of vertical, the concentration of C-axis crystal was observed to decrease by about two thirds.

Further X-ray camera modification is in progress to allow scanning of crystallite orientation over a much larger angle from the vertical; methods of mathematical evaluation of the X-ray data are also being developed.

The degree of crystallinity of partial size is perhaps of even greater interest, but may be more difficult to measure quantitatively. Various CdS powders were also X-rayed for comparison of both comparative and absolute diffraction intensities. The G.E. 118-8-2 Luminescent Grade CdS powder gives diffraction intensities comparable to evaporated thin films, while sintered polycrystalline CdS is several times more intense. Interestingly, the spray-coated CdS films show an X-ray intensity comparable to coarsely crystalline material.

When observed with a polarizing microscope, both the evaporated films and the sprayed films showed broadly uniform birefringence; however, when the vacuum evaporated film is split off the glass, most of this birefringence disappears. When observed microscopically, the individual crystallite size appears to be of the order of one to 10 microns across.

Critical examination of the X-ray data thus far shows no detectable amount of β -phase (cubic zinc blende structure) CdS in any of the films so far studied.

6. WORK PLANNED FOR NEXT QUARTER

In the next quarter, work will continue in general along the lines discussed in this report. Electrical measurements will be expanded to include those described in Section 3.4, optical measurements will include spectral response and intensity dependency.

Evaporation parameters will continue to be studied as will the Cu_2O slurry process. Some attention will be given to producing high efficiency single crystal cells as controls for the film cells. The "wet chemistry" approach will continue at about the same level; the film structure studies will be vigorously pursued.

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8. PERSONNEL

Time devoted to this project by principal technical personnel and others in the period January 1, through March 31, 1963, follows:

		<u>Hours</u>
W. J. Deshotels	Project Scientist	496
F. Augustine	Senior Chemist	504
A. E. Carlson	Senior Physical Chemist	139
M. P. Makowski	Senior Chemist	428
Others	(Mostly Technicians)	1290
	Total	<u>2857</u>

9. EXPENDITURES

Actual Costs, October 1, 1962 through March 31, 1963	\$54,000.00
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